

A SEARCH FOR INTERSTELLAR PYRROLE: EVIDENCE THAT RINGS ARE LESS ABUNDANT THAN CHAINS

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ABSTRACT

Searches for three transitions of pyrrole (C_4H_5N) give maximum column density $N_{\max} = 3\text{--}10 \times 10^{13} \text{ cm}^{-2}$ in Sgr B2. This limit is more than 10 times lower than previous ring molecule limits, and is slightly lower than column densities of known interstellar molecules with from four to six heavy atoms.

Subject headings: galaxies: nuclei — interstellar: molecules — line identifications

I. INTRODUCTION

Planar conjugated rings with a skeleton of three or more heavy atoms (C, N, O, or S) are fundamental building blocks in biological and industrial chemistry, and tend to be extremely stable molecules. A major puzzle is why none has been detected in interstellar clouds, where many molecules comparable in size and weight to the simpler rings have already been found. Without exception, the backbone of the known interstellar molecules is a simple linear chain. Whether this reflects a fundamental barrier to the production of rings in the interstellar medium, or is instead a selective effect is unknown. Chains have simpler rotational spectra and partition functions than rings, and atom for atom are somewhat easier to detect at radio frequencies.

The rings which radio astronomers have attempted to find include furan and imidazole (de Zafra *et al.* 1971), fulvene (Giguere *et al.* 1973), pyridine and pyrimidine (Simon and Simon 1973), and cyclobutanone and the benzene derivatives benzonitrile, benzaldehyde, toluene, and nitrobenzene (Fertel and Turner 1975). The limits set on the column densities of these rings in molecular clouds are not particularly low, being generally larger than 10^{15} cm^{-2} . In this paper we report a sensitive but unsuccessful search for pyrrole, C_4H_5N , a stable five-membered ring which is a constituent of two famous organic pigments, hemoglobin and chlorophyll. Analysis of the limits set on three rotational transitions in Sgr B2 yields a column density of less than $3\text{--}10 \times 10^{13} \text{ cm}^{-2}$ —a result which is fairly insensitive to the rotational excitation assumed for pyrrole. This limit is lower by a factor of 10 or more than previous limits on the column density of interstellar rings, and is comparable to or lower than

column densities of known linear molecules in Sgr B2 with from four to six heavy atoms.

II. EQUIPMENT AND RESULTS

Our observations were made at the frequencies of the $9_{09} \rightarrow 8_{08}$ (86,109 MHz), the $8_{08} \rightarrow 7_{07}$ (77,045 MHz) and the $1_{10} \rightarrow 1_{11}$ (4469 MHz) pyrrole rotational transitions. Frequencies were calculated from rotation constants which Nygaard *et al.* (1968) derived from conventional microwave spectroscopy. Uncertainties in frequency due to uncertainties in the rotation constants, and to neglect of centrifugal distortion, are generally smaller than the spectral resolutions of the spectrometers used in our astronomical search.

The two higher frequency transitions were sought in 1978 with the 7 m telescope of the Bell Telephone Laboratories at Holmdel, New Jersey. The receiver was a cooled mixer radiometer with a single-sideband noise temperature of 350 K (Linke, Schneider, and Cho 1978). Intensity calibration was done with a chopper-wheel and hot (~ 300 K) and cold (77 K) loads. The main beam width (FWHM) was ~ 2.5 . The spectrometer was a filter bank of 512 channels, each 1 MHz wide. The observations were made using position switching.

The 4469 MHz transition was sought in 1979 September with a cooled, dual-channel parametric amplifier receiver at the prime focus of the 42.7 m telescope of the National Radio Astronomy Observatory² in Green Bank, West Virginia. The two channels received orthogonal linear polarizations; each had a system temperature of 70–90 K on cold sky. Intensity calibration was done with a noise diode. At 4469 MHz

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the angular resolution (FWHM) of the telescope is 6'.7, and its beam efficiency is 0.76. The spectrometer was a 384-channel digital autocorrelator. In the $1_{10} \rightarrow 1_{11}$ pyrrole transition, the hyperfine structure produced by the N nucleus is large compared to the expected line width in all sources; for all sources (except TMC-1) we therefore worked with a bandwidth of 10 MHz, frequency switching by 5 MHz. The autocorrelator was used in the parallel mode as two independent 192-channel spectrometers, each with spectral resolution 63 kHz (4.2 km s^{-1}). The two resulting spectra were averaged together. In TMC-1, lines are very narrow (0.5 km s^{-1}), so we worked with a bandwidth of 1.25 MHz in the series correlator mode. The spectral resolution was then 3.9 kHz (0.26 km s^{-1}). This 1.25 MHz bandwidth includes the frequencies of the $F = 2 \rightarrow 1$, $1 \rightarrow 0$, and $2 \rightarrow 2$ hyperfine components, having frequency shifts from $4469.26 \pm 0.02 \text{ MHz}$ of -0.17 , -0.06 , and 0.19 MHz , respectively, and having relative intensities of 13.9, 11.1, and 41.7% in the optically thin LTE case. The $F = 2 \rightarrow 2$ is the strongest allowed transition.

A summary of our attempts to detect pyrrole is given in Tables 1 and 2. The spectra were smoothed to an effective resolution approximately one-third of the expected line width. The upper limits on the line radiation temperatures T_R listed in Tables 1 and 2 are 3σ limits on the antenna temperature, corrected for beam efficiency, and assuming as usual that the source fills the beam. For each source and transition, the limit on T_R was converted to a limit on column density, N_{\max} , in the following way: The transition was first assumed to be optically thin. The maximum column density in the transition initial state was then calculated for specific transition excitation temperatures T_{ex} by assuming (1) a line width equal to that of other lines in the source (20 km s^{-1} for Sgr B2); (2) a background brightness temperature of 2.8 K at 4 mm; (3) a background brightness temperature at 6 cm based on source measurements by Reifstein *et al.* (1970). For the 6 cm transition the hyperfine splitting was accounted for by assuming normal (optically thin) LTE relative intensities as described above. The initial-state column density limit was converted to a total column density limit N_{\max} on the assumptions of rotational

TABLE 1
LIMITS ON PYRROLE LINES IN SAGITTARIUS B2^a

TRANSITION	REST FREQUENCY (MHz)	UPPER LIMIT ON T_R (K)	N_{\max} (10^{13} cm^{-2})		
			5 K ^b	15 K ^b	30 K ^b
$9_{09} \rightarrow 8_{08} \dots$	86109	0.02	52	7	8
$8_{08} \rightarrow 7_{07} \dots$	77045	0.05	64	16	23
$1_{10} \rightarrow 1_{11} \dots$	4469	0.005	3–10 ^c	440	1200

^a $\alpha(1950) = 17^{\text{h}}44^{\text{m}}11^{\text{s}}$, $\delta(1950) = -28^{\circ}22'30''$.

^b T_{rot} .

^c Sensitive to small departures from rotational equilibrium: the smaller value given here corresponds to $T_{\text{ex}} = 2 \text{ K}$; the larger, to $T_{\text{ex}} = 5 \text{ K}$.

equilibrium and a classical partition function (the double pair of protons in pyrrole gives rise to symmetric and antisymmetric spin statistical weights of 10 and 6; this has a 25% effect on fractional populations, an effect which was taken into account).

Upper limits on column densities derived in this way are given in Table 1 for Sgr B2 and in Table 2 for other sources. The lowest value of N_{\max} in Sgr B2, $3 \times 10^{13} \text{ cm}^{-2}$, derives from the missing $1_{10} \leftarrow 1_{11}$ line on the assumption $T_{\text{ex}} = 2 \text{ K}$, $T_{\text{rot}} = 5 \text{ K}$. This case was considered in the event that pyrrole, like formaldehyde, has anomalously high population in the 1_{11} level. At the higher temperatures $T_{\text{rot}} = 15 \text{ K}$ and 30 K , the pyrrole column density is constrained to low values of $N_{\max} = 7 \times 10^{13} \text{ cm}^{-2}$ and $8 \times 10^{13} \text{ cm}^{-2}$ by the $9_{09} \rightarrow 8_{08}$ limit. Taken together, these cases yield for Sgr B2 a limiting column density $N_{\max} = 3\text{--}10 \times 10^{13} \text{ cm}^{-2}$. The $1_{10} \rightarrow 1_{11}$ limits for other sources in Table 2 are considerably higher, since this transition is strong only at low rotational temperatures, i.e., $T_{\text{rot}} \lesssim 5 \text{ K}$. We note that recent observations at the $2_{02} \rightarrow 1_{01}$ pyrrole transition frequency of 22.7 GHz give a radiation temperature upper limit of 0.02 K toward TMC-1 (Kutner *et al.* 1980). Using the same assumptions as described previously, we deduce $N_{\max} \sim 3 \times 10^{13} \text{ cm}^{-2}$, a number comparable to our limit in Sgr B2. Therefore the apparent deficiency of pyrrole with respect to comparable chains in Sgr B2, discussed in § III, may also extend to TMC-1.

TABLE 2
LIMITS ON THE $1_{10} \rightarrow 1_{11}$ LINE OF PYRROLE IN OTHER SOURCES

Source	$\alpha(1950)$	$\delta(1950)$	Upper Limit on T_R (K)	T_{rot} ^a (K)	N_{\max} (cm^{-2})
TMC-1	04 ^h 38 ^m 42 ^s	25°35'45"	0.08	15	3×10^{14}
OMC-1	05 32 47	−05 24 20	0.03	70	7×10^{15}
IRC 10216	09 45 15	13 30 40	0.03	100	7×10^{16}
W51	19 21 23	14 24 28	0.02	50	1×10^{16}

^a Assumed on the basis of other molecular observations.

III. DISCUSSION

The present value of N_{max} for pyrrole is lower by a factor of at least 10 than previous limits on interstellar rings. However, it is difficult to estimate whether this limit is significantly lower than the column density of linear molecules of comparable complexity. One basis of comparison is simply the number of heavy atoms per molecule. There is no known interstellar molecule which, like pyrrole, has five heavy atoms, but there are several with four and there is one with six. Let us consider cyanoacetylene (HC_3N : Morris *et al.* 1976), vinyl cyanide (CH_2CHCN : Johnson *et al.* 1977), ethyl cyanide ($\text{CH}_3\text{CH}_2\text{CN}$: Johnson *et al.* 1977), and methyl formate (CH_3OOCH : Cummins and Thaddeus 1980), whose column densities are respectively $N = 20, 3, 9$, and 16 cm^{-2} , all $\times 10^{13} \text{ cm}^{-2}$. The one molecule with six heavy atoms known in Sgr B2 is HC_5N , with $N = 16 \times 10^{13} \text{ cm}^{-2}$, according to Avery *et al.* (1979). These column densities are comparable to or greater than our upper limit on pyrrole. For the first time we have evidence for an actual deficiency of a ring with respect to comparable chains.

If rings are generally less abundant than chains, it may be possible to restrict the types of reactions that are effective in producing interstellar molecules (de Zafra *et al.* 1971; Fertel and Turner 1975). According to Fertel and Turner (1975), chemistry on the surface of interstellar grains may produce both rings and

chains, while gas phase reactions are likely to yield chains alone. A deficiency of rings may therefore imply that grain surface chemistry is unimportant in the production of the larger interstellar molecules. There are clearly loopholes in this argument—no one yet knows the efficiency of ring production on grains. But it does suggest that progressively more sensitive searches for interstellar rings, and detailed predictions of their abundance, may be of value to our understanding of interstellar chemistry.

In summary, we have found that the upper limit on the pyrrole column density in Sgr B2 is less than, or comparable to, the column density of known linear molecules with a similar number of heavy atoms. For reasons of receiver sensitivity, we believe it will be difficult in the near term to significantly improve the pyrrole limits for Sgr B2 which we set here. Work on other molecules remains to be done, however. In particular, adequate searches have not been reported for the three-membered rings ethylene oxide and ethylenimine. Because of the favorable partition functions of these simple rings, they are potentially good candidates for interstellar detection.

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